values of $\psi_{1/2}$ for planar channeling decrease much more rapidly with decreasing planar spacing than predicted by Eq. (4).

The observed values of the axial minimum yield (a measure of the unchanneled fraction of the beam) agree well with the theoretical estimates in the case of C (diamond), Si, Ge, and GaP lattices. In GaAs and GaSb, however, the observed values are significantly larger than expected; this is attributed to the influence of oxide layers, surface contamination or lattice imperfections.

Note added in proof: More detailed calculations which include the effect of surface transmission show agreement with the experimentally observed $\psi_{1/2}$ dependence on planar spacing. Results to be published by S. T. Picraux and J. U. Andersen.

ACKNOWLEDGMENTS

We are indebted to Dr. F. Trumbore for supplying the GaP samples, and to Dr. J. McNeely for the GaAs and GaSb samples. We particularly want to thank Ian Mitchell for his participation in the x-ray measurements and in their subsequent interpretation. The assistance of G. R. Bellavance and G. A. Sims with the Van de Graaff bombardments and of P. Kjær with the 50-keV H^+ measurements is also gratefully acknowledged.

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Impurities and Secondary Reactions in Radiation Defect Production at Liquid-Nitrogen Temperature in Alkali Halides*

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The F-center production rate due to electron irradiation at 80°K has been measured in pure KCl and KBr, in KCl doped with Ag, Ca, Cd, Co, and Tl, and in KBr doped with Ca and Cl. In every case an enhancement of the defect production rate was observed in samples containing between 1 and 100 ppm impurity. Accompanying the enhancement of the F-center production rate was a saturating growth of ultraviolet absorption, usually in the V_1 region of the spectrum, and a temporary suppression of the growth of the intrinsic ultraviolet absorption band (240 nm for KCl and 275 nm for KBr, sometimes labeled V_4). In KCl samples containing more than 100 ppm impurity, the 240-nm band was observed to shift to shorter wavelengths. In addition, the stability of the defects produced in doped samples was found to be less upon warming or bleaching than that of pure samples. The F-center growth curves have been compared with predictions of a model in which free interstitials can either recombine with vacancies or be trapped by defects. The curve shapes suggest that the model in its simplest form is not valid, and that perhaps most of the interstitials and vacancies remain correlated.

I. INTRODUCTION

In a recent study[1] of color center production at liquid-nitrogen temperature it was found that lead impurity could significantly enhance the rate of F-center formation. It was suggested in that work that the lead acted as a trap for mobile interstitial defects and thus enhanced the colorability by impeding the recombination of defects.

Whether the complicated radiation damage behavior of alkali halides at temperatures above the liquid-helium range is due to a number of different production processes or is simply due to recombination and other secondary reactions following one efficient primary production mechanism[2] is a rather basic question.[3] For this reason we felt that a more extended study of the influence of impurities on defect production at liquid-nitrogen temperature would be useful. In particular, we wanted to test the suggestion that interstitial trapping impedes recombination of interstitials and vacancies. Therefore, we decided to irradiate at liquid-nitrogen temperature, where interstitials in KCl are mobile, and to see whether the enhancement of defect production that had been observed for lead doping[1] could also be found in KCl doped with impurities of different valence and size. We present here results of investigating KCl(Ag) rather extensively and KCl(Ca), KCl(Tl), KCl(Co), and KCl(Cd) in a more rudimentary fashion. We also report a few results obtained with doped KBr.

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* Work supported in part by the U. S. Atomic Energy Commission.

† Guest scientist from Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

[1] E. Sonder and W. A. Sibley, Phys. Rev. **140**, A539 (1965).

[2] D. Pooley, Proc. Phys. Soc. (London) **87**, 245 (1966); H. N. Hersh, Phys. Rev. **148**, 928 (1966).

[3] For a review of the history and recent work connected with this problem, see J. H. Crawford, Jr., Advan. Phys. **17**, 93 (1968); see also Refs. 1, 14, 15, and J. H. Crawford, Jr., W. A. Sibley, and E. Sonder, Phys. Status Solidi **23**, 301 (1967).

TABLE I. List of samples, their sources and impurities.

Ingot designation	Source[a]	Dopant	Concentration (ppm M)	Impurities detected in crystals[c] (ppm M) Na[b]	Rb	Br	I	N	S
0302	*B*	...		1	1	1	2	2	<1
0227	*B*	...		2		3			
1223	*S*	Ag	0.7	6		1			
1116	*S*	Ag	7.6	2	$<\frac{1}{2}$	1	<1	<1	<1
1221	*S*	Ag	20	1	$<\frac{1}{2}$	1	<1	<1	1
1118	*S*	Ag	62	1	$<\frac{1}{2}$	1	2	<1	<1
0413	*S*	Ca	~1	2	1				
0613	*S*	Ca	~80	1	3	35	6	90	10
0424	*S*	Tl	0.2	2	$<\frac{1}{2}$				
Y-1	*Y*	Tl	40						
C-1	*C*	Co	80						
C-2	*C*	Cd	25						
W-1	*W*	...							
R-1	*R*	Cl	~3000						
R-2	*R*	Ca	~100						

[a] *B*, C. T. Butler, research materials group, Oak Ridge National Laboratory (see Ref. 4); *S*, grown as described in text, except for ingot 0613, which was grown from commercial starting material [see W. A. Sibley and J. R. Russell, J. Appl. Phys. **36**, 810 (1965)]; *Y*, P. H. Yuster, Argonne National Laboratory; *C*, R. Cappelletti, University of Parma; *W*, R. Warren, Westinghouse; *R*, B. S. H. Royce, Princeton University.

[b] Probably all sodium determinations are high due to sodium in the surroundings.

[c] Tests for other impurities such as Li, Mg, Al, Si, P, Fe, Cu, Cs, and Pt were invariably negative. Methods used were generally sensitive to 1 ppm.

II. EXPERIMENTAL

A. Crystal Preparation

The KCl starting material we used was highly purified by recrystallization, extraction, and treatment with Cl_2 and HCl gases.[4] To a solid polycrystalline mass of this purified KCl was added the dopant in the form of "chem pure" chloride. This mixture was then heated slowly to approximately 550°C and baked there under high vacuum. Then the system was filled with N_2 gas and sealed; the temperature was then raised to melt the mixture and permit dipping a seed and pulling a single-crystal ingot. The resulting ingots, weighing between 100 and 200 g, were analyzed; it was found that trace impurities other than the dopant were little greater than in the starting material, being less than the detectable limit of approximately 1 ppm for most impurities. In Table I we list the ingots prepared for the present study together with their impurity content. We also list samples from ingots grown elsewhere. The dopant concentrations in the crystals grown by us usually varied by a factor of 3 in the approximately 10 cm length of crystal. For Ag- and Ca-doped samples the impurity content was greater in that part of the crystal which was grown later, as one would expect. For Tl, however, the dopant content decreased in later grown sections of the ingot, suggesting that Tl is lost by evaporation or precipitation from the melt.

B. Impurity Content of Samples

Experimental samples were cleaved from the ingots to about $1\frac{1}{2}$ cm×1 cm×0.25 mm. Where possible, the impurity content was determined for the sample itself by measuring the heights of the ultraviolet impurity absorption bands. For Ag we determined the relation between the heights of the bands and the silver content in auxiliary measurements on samples large enough to permit reasonably accurate chemical analyses. Plots of the heights of the three normal appearing silver bands versus impurity content are reproduced in Fig. 1. The error bars shown for low and high concentration in the figure are an estimate of the accuracy of the chemical analysis and the precision of estimating the height of the impurity bands above the base line for undoped KCl. For Tl doping we analyzed only one sample. This sample contained 120/(μg Tl)/(g KCl) and exhibited a 248-nm Tl band that had a maximum absorption coefficient of 30 cm^{-1}. Our ratio of Tl content to band height was within 10% of the more extensive results in

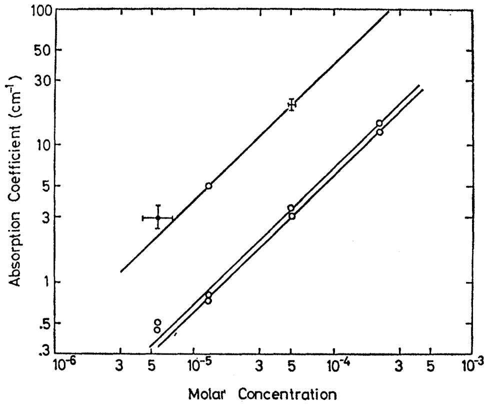

FIG. 1. Peak absorption coefficient at room temperature for silver-impurity absorption bands in KCl versus silver concentration. The three curves are, from top to bottom, for the 196-, 216-, and 228-nm bands, respectively. No attempt has been made to obtain the height of the resolved bands; absorption coefficients have simply been measured at the peak positions with respect to the base line obtained with an undoped sample.

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[4] C. T. Butler, J. R. Russell, R. B. Quincy, Jr., and D. E. LaValle, J. Chem. Phys. **45**, 968 (1966).

the literature[5]; these also indicated that the 248-nm band is indeed approximately proportional to the Tl content. For samples doped with other impurities, the values we give are estimates obtained from analyses of material from the same section of the ingot as the samples used.

C. Irradiation of Specimens

The radiation procedure and techniques were similar to those described previously.[1,6] A calibration of the energy absorbed by a sample from the electron beam was obtained by measuring the heating rate at the start of irradiation of an isolated sample of KCl containing a thermocouple. We found that with the cryostat 20 cm from the end window of the accelerator and a total current of 20 μA, the energy deposition rate was $(1.6\pm0.2)\times10^{18}$ eV/cm^3 sec. It should be pointed out that for the previously measured lead-doped KCl, a different accelerator and a different calibration procedure were used. In Fig. 2 we show a comparison of two samples from the same ingot irradiated with the two facilities. The difference between the curves is well within the accuracy of the energy deposition rate calibrations, giving evidence that the absolute values of energy absorbed by the samples are significant and that within a possible error of about 20% intercomparison between the present work and the lead results can be made. The 20% figure refers to the absolute calibration. Since the electron current was measured and integrated during all irradiations, relative errors are no more than 5%.

F-center concentrations for both KCl and KBr were calculated by multiplying the *F*-band peak absorption coefficient by 2.5×10^{15} (*F* centers)/cm^3 per cm^{-1}. This factor is made up of the various constants appearing in the Smakula equation, including the half-width and oscillator strength, and has an uncertainty of about 10%.

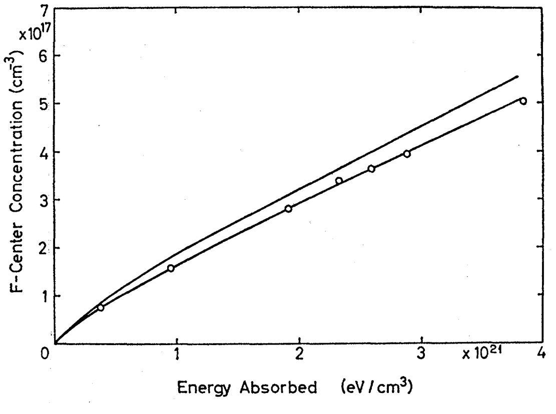

FIG. 2. Comparison of *F*-center production curves obtained with the Ispra and with the Oak Ridge electron Van de Graaff. The upper curve is a reproduction of one appearing in Ref. 1; the lower curve was obtained with a sample from the same crystal (0227) using the Ispra facility.

III. RESULTS

A. Influence of Silver on *F*-Center Production

In Fig. 3 we have plotted the *F*-center concentration produced by electron irradiation of pure and silver-doped samples of KCl. Approximately 1 ppm Ag causes a noticeable enhancement, and this enhancement becomes greater for amounts of silver up to about 20 ppm. For amounts greater than that, as shown by the dashed curve in the figure, the initial *F*-center production becomes smaller, but the curves have an initial positive curvature. This behavior is very similar to that found for lead impurities. The enhancement is of the same magnitude and occurs for the same impurity concentration range. The positive curvature that was apparent in quenched, heavily lead-doped KCl (>150 ppm) can also be observed in silver-doped KCl.

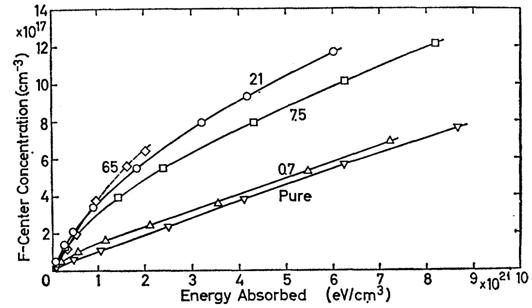

FIG. 3. Production of *F* centers in pure and silver-doped KCl irradiated at 80°K. The abcissa scale refers to the energy absorbed by the sample from the electron beam. The numbers next to each curve give the silver content of the samples in *M* ppm.

More important, as was also the case in lead-doped KCl, silver impurities of the order of 5–10 ppm produce considerably more than one *F* center per impurity. For example, comparison of the $7\frac{1}{2}$-ppm and the pure sample shows that after an irradiation of 8×10^{21} eV/cm^3, 28-ppm more *F* centers are produced in the doped sample. This is almost four *F* centers for every impurity ion.

The great similarity in behavior of (monovalent) silver-doped KCl and (divalent) lead-doped material made us think that perhaps the influence of impurities on the *F*-center production rate was not related to the chemical properties of the dopant. We therefore investigated in a more superficial fashion the effect of a number of other dopants in KCl and KBr.

B. Other Impurities in KCl and KBr

Figure 4 shows that the enhancement of *F*-center production observed is quite general and occurs also in KCl doped with Ca, Cd, Co, or Tl. We also observed a small enhancement in a pure KCl sample that had been

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[5] W. Koch, Z. Physik **57**, 638 (1929).

[6] W. A. Sibley, E. Sonder, and C. T. Butler, Phys. Rev. **136**, A537 (1964); E. Sonder and W. A. Sibley, *ibid.* **129**, 1578 (1963).

heated to 480°C in air for 5 h. It is known that in a sample so heated, the luminescence changes and increases,[7] as does the room-temperature colorability.[8] This is presumably due to diffusion doping with oxygen, nitrogen, or OH during the heat treatment. It is interesting that a nonmetallic impurity produces a similar enhancement of radiation defect production as do metallic impurities.

The increase in defect production rate due to impurities can also be observed in KBr irradiated at 80°K. We were able to obtain a piece of zone-refined KBr and two pieces doped with rather large amounts of Ca and Cl, respectively. Figure 5 shows coloration curves for these materials. Since even in the zone-refined sample a significant absorption in the V_k-V_1 region appeared, we suspect that all these KBr samples contain small amounts of either electron-trapping impurities (to produce V_k centers) or foreign alkali ions (to produce V_1 centers).[9] However, the doped samples contained enough of the added impurities so that the observed enhancement can probably be attributed to the dopants rather than to other unknown trace contaminants.

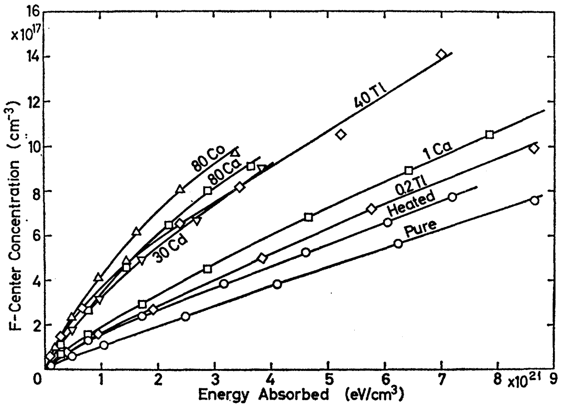

FIG. 4. Radiation production of F centers in KCl doped with various impurities. The numbers and chemical symbols labeling the curves give concentrations in M ppm and species of impurities. The curve labeled "heated" is for a sample from a pure crystal (0302) that had been heated in air for 5 h. Sample temperatures were 80°K during irradiation and measurement.

C. Radiation-Produced Ultraviolet Bands

Upon first glance the ultraviolet bands produced in KCl appeared to vary in an inexplicable fashion with impurity and dose. However, upon studying the growth rates of these bands we were able to find a consistent pattern. Apparently the reason for the complexity is that three types of centers contribute to the ultraviolet absorption. These we shall call charge-transfer centers, nonsaturating centers, and saturating centers.

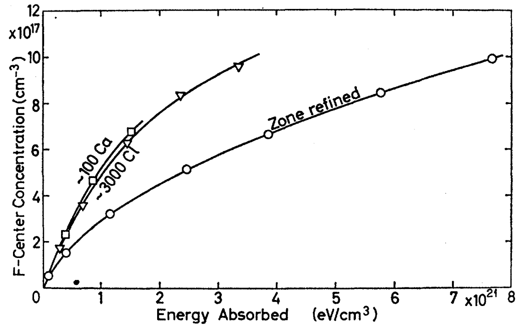

FIG. 5. Production of F centers in zone-refined and doped KBr irradiated at 80°K. Curves for chlorine and calcium doping are shown. The numbers are estimates (in ppm M), from chemical analyses of the impurity content.

The first are simply electrons or holes that are trapped. For instance, an electron trapped at a silver ion produces a band at 420 nm[10]; a self-trapped hole produces a V_k band. We can recognize these centers rather easily because charge transfer is extremely rapid, and band heights saturate almost immediately at the dose rates used in these experiments. Bands due to what we call nonsaturating centers are usually broad and, for long irradiations, grow indefinitely and approximately linearly with the F band. Bands of saturating centers are not proportional to the F band but begin to saturate after moderate irradiations. These centers undoubtedly include impurities initially present. In Fig. 6 we show examples of the growth versus that of the F band for the three types of centers.

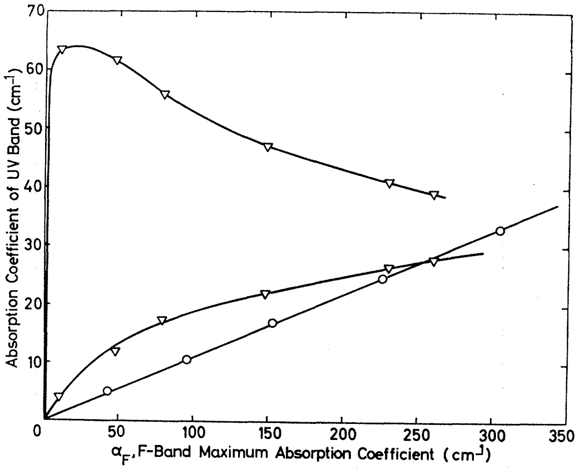

FIG. 6. Growth of three types of ultraviolet absorption bands versus the growth of the F band during electron irradiation. The linear curve with the circular point symbols is for the 240-nm band in undoped KCl. The other two curves were observed in silver-doped KCl. The upper one is for the 420-nm Ag^0 band; the lower one is for the band peaking at 223 nm, which is depicted as a dashed line in Fig. 7.

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[7] A. Halperin and N. Lewis, Phys. Rev. **119**, 510 (1960).

[8] W. A. Sibley, Phys. Rev. **133**, A1176 (1964).

[9] J. L. Kolopus, C. J. Delbecq, D. Schoemaker, and P. H. Yuster, Bull. Am. Phys. Soc. **12**, 467 (1967).

[10] C. J. Delbecq, W. Hayes, M. C. M. O'Brian, and P. H. Yuster, Proc. Roy. Soc. (London) **271A**, 243 (1963).

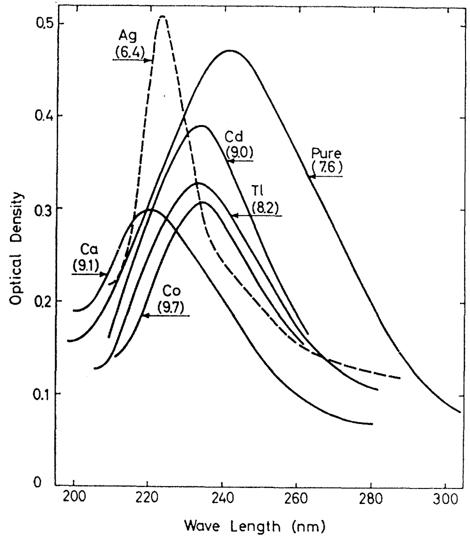

FIG. 7. Ultraviolet bands produced in KCl by heavy irradiation at 80°K. Except for the curve labeled "pure," the curves are for the most heavily doped samples of the respective impurities (see Table I). The number below the impurity labels refers to the F-center content (in units of $10^{17}/\text{cm}^3$) at the time the spectra shown were observed.

Except for the most heavily silver-doped KCl, we found that prolonged heavy irradiation produced for each sample one chief band of the nonsaturating type. In pure KCl and material doped with less than 10-ppm impurity, this band peaked very close to 240 nm.[11] In heavily doped material, the band appeared shifted to shorter wavelengths. In Fig. 7 we have reproduced, using solid lines, spectra of these nonsaturating bands for a number of different impurities. The exact position of the peaks of these bands may not have very much significance. We found, for instance, that for the 100-ppm calcium-doped sample the peak appeared at 220 nm. For a sample from a less heavily doped section of the same ingot we found[1] that for comparable irradiation the band peaked at 225 nm. A look at Table I will show that this ingot contained impurities other thanCa. Thus, such a shift may stem from different impurities or from a difference in concentration of Ca. Also, we found in some lightly doped samples that the band initially peaked at wavelengths shorter than 240, shifting to 240 after longer irradiation.

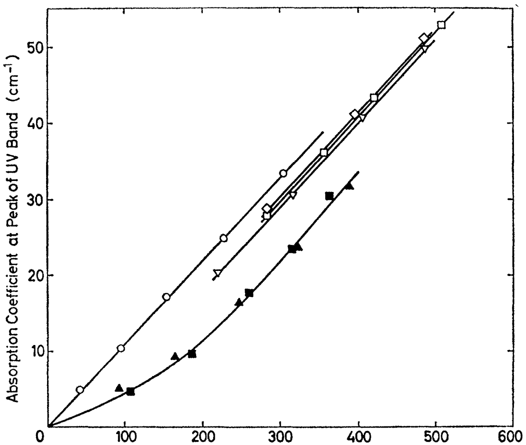

FIG. 8. Growth of the nonsaturating ultraviolet absorption versus growth of the F band during electron irradiation of KCl. The open symbols are for pure or lightly doped material for which the ultraviolet band peaks at 240 nm. The closed point symbols are for heavily doped samples for which the peak is at shorter wavelengths. For the various impurities the point symbols are as follows: ○, undoped KCl; ◇, Tl; □, Ca; ▽, Ag; △, Co.

In Fig. 8 we show how these nonsaturating bands grow with respect to the F band. It is noteworthy that the straight line relating the height of the 240-nm band and the F band in pure KCl can be extrapolated back through the origin, but that for even lightly doped samples the initial growth of the F band is unaccompanied by a proportional growth of the 240-nm band. This is even more evident for the heavily Co- and Ca-doped samples. For these we found a very slow initial growth of the nonsaturating ultraviolet bands with respect to the F bands, as can be seen in Fig. 8.

This delay in the onset of growth of nonsaturating bands was normally accompanied by growth of saturating bands. For Ca-, Cd-, Co-, and Tl-doped KCl this absorption appeared in the vicinity of the V_k and V_1 bands and changed shape and position as the irradiation progressed. Thus, it is difficult to know clearly how much of the absorption in the V_1-V_k region was due to simple charge trapping and how much of it was due to saturating centers involving radiation-produced ionic defects (e.g., V_1-like centers).

In heavily silver-doped KCl, it was difficult to observe a nonsaturating band even after rather heavy irradiation [$6\frac{1}{2}\times10^{17}$ (F centers)/cm^3]. Instead, there appeared a narrower band with a peak at 223 nm. The growth of this band was not proportional to the growth of the F band. Its spectrum and growth curve are reproduced in Figs. 7 (dashed curve) and 6, respectively. In Fig. 7 a shoulder can be observed on the long-wavelength side of the band. The band and its shoulder are difficult to resolve quantitatively; however, we were able to determine that the shoulder did not exhibit the strong saturating character that was exhibited by the 223-nm band. Moreover, the shoulder band was broad, comparable in width to the 240-nm band of the pure KCl.

The behavior of the ultraviolet absorption in doped KBr was similar to that found for KCl. Figure 9(b) shows that in Cl- and Ca-doped material the V_4 band[12] initially grows less rapidly with respect to the F band than it does in zone-refined material. We even found evidence of a delay in V_4-band production in the zone-

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[11] This is undoubtedly the same band reported by B. J. Farady and W. D. Compton, Phys. Rev. 138, A893 (1965).

[12] J. D. Kingsley, J. Phys. Chem. Solids 23, 949 (1962).

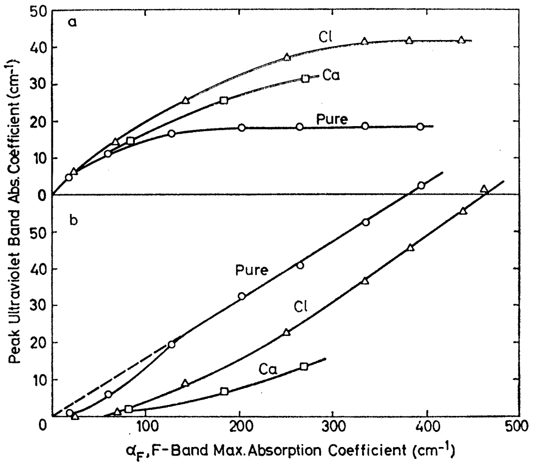

FIG. 9. Growth of ultraviolet absorption versus growth of the F band during electron irradiation of KBr. (a) Growth of saturating bands in the V_1-band region of the spectrum. (b) Growth of the V_4 (275-nm) band.

refined sample. As was also the case for KCl, the delay was accompanied by saturating growth in the V_1-band (410-nm) region. This is clearly evident in the curves for the pure and Cl-doped KBr samples depicted in Fig. 9(a).

The position of the V_4 band does not vary as much with doping as does that of the 240-nm band in KCl. The peak positions are 276, 276, and 273 nm for the zone-refined, Cl-doped, and Ca-doped samples. Without more careful work, it is not possible to decide whether the apparent shift in the Ca-doped sample is real.[13]

Data such as those reported herein have recently been reported for pure and Ca-doped KBr by Itoh and Ikeya.[14] Although they irradiated at dry-ice temperature and worked with F-center concentrations approximately a factor of 5 below those used in the present work, it is of interest to compare the results. Itoh and Ikeya found that at dry-ice temperature doping caused the V_4 band to be replaced by a band peaking at shorter wavelengths, i.e., the D_3 band peaking at 266 nm. They were able to observe the cessation of D_3-band growth and a commencement of V_4-band growth in lightly doped KBr when the number of F centers produced was equal to the number of Ca ions. From this they reasoned that the D_3 band was produced when an interstitial was trapped at a divalent cation-vacancy complex. (This is the model originally proposed by Hayes and Nichols[15] for a band peaking at 355 nm.) These results are closely analogous to our KCl results, and it is tempting to attribute the shifted nonsaturating bands that we find to interstitials trapped at divalent ion-vacancy complexes. However, the fact that we also observe such a shifted band for monovalent impurity doping (see the curve in Fig. 7 for KCl:Tl), suggests that interstitials may also be trapped at other defects. Moreover, the absence of any turning down or saturation of the ultraviolet-band growth curves shown in Fig. 8, even when the F-center concentration is equal to and exceeds the dopant concentration, suggests that the impurities do not trap one single interstitial as would be predicted by the model used for the KBr D_3 band.

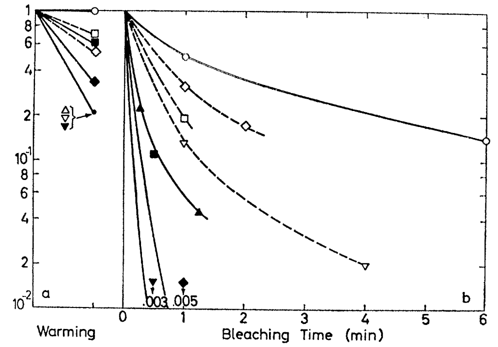

FIG. 10. Disappearance of radiation-produced F centers (a) upon warming and (b) upon room-temperature bleaching. The curves are normalized to the F-center concentration before warming or bleaching, respectively. The different point symbols refer to light (open symbols) and heavy (closed symbols) doping with the following impurities: ◇, Tl; □, Ca; ▽, Ag (7.6 and 62 ppm); △, Co; ○, undoped KCl.

Itoh and Ikeya also report the production of a significant 355-nm band[15] and little absorption in the V_1 region. We found, to the contrary, that irradiation at 80°K produced very few centers absorbing at 355 but significant absorption in the V_1-V_k region. This difference is probably due to differing stabilities or production efficiencies of these ultraviolet absorbing centers, the irradiations being performed at different temperatures.

D. Stability of Radiation-Produced Defects

Figure 10 shows the disappearance[16] of F centers in KCl upon warming from 80°K to room temperature [Fig. 10(a)] and upon subsequent bleaching with white light [Fig. 10(b)]. Dashed lines connect the data points for lightly doped samples, while solid lines are used for the pure and the heavily doped material. It is clear that radiation defects in pure KCl are much more resistant to warming and to room-temperature bleaching than are those produced in doped material. It should be pointed

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[13] B. J. Farady and W. D. Compton (Ref. 11) report that an apparent shift in the V_4-band position may result from admixture of a saturating band whose peak is at 254 nm.

[14] N. Itoh and M. Ikeya, J. Phys. Soc. Japan 22, 1170 (1967).

[15] W. Hayes and C. M. Nichols, Phys. Rev. 117, 993 (1960).

[16] We are assuming in this discussion that F centers produced by irradiation at liquid-nitrogen temperature disappear primarily by recombination with interstitials. This is based on the following considerations: (a) α centers and F' centers are not observable at room temperature; (b) the disappearance of the F band is accompanied by a corresponding and total disappearance of the ultraviolet absorption; (c) it was found in previous work [W. A. Sibley and E. Sonder, Phys. Rev. Letters **14**, 900 (1965)] that warming to room temperature followed by bleaching caused not only the absorption bands but also the radiation-induced hardening to disappear. Moreover, we have observed that re-irradiation of such bleached samples produces coloring curves substantially identical to those produced in virgin samples.

out in addition that, even in pure KCl irradiated at 80°K, the radiation defects are very much *less* stable than are defects produced by irradiating at higher temperatures.[17]

In KBr, both the zone-refined and the Cl-doped samples lose 90% of the radiation-produced F centers upon warming to room temperature. Defects remaining at room temperature are more difficult to bleach in zone-refined material than in doped KBr.

IV. SUMMARY OF OBSERVATIONS

The behavior of pure and doped KCl and KBr irradiated at 80°K can be summarized as follows:

(a) Impurities of approximately 5–100 ppm cause the defect production to be significantly enhanced. This enhancement appears to be insensitive to the chemical properties of the impurity.

(b) The number of excess F centers produced in a doped as compared with an undoped sample is greater than the impurity concentration.

(c) The nonsaturating ultraviolet bands change little for light doping; in heavily doped KCl they shift to shorter wavelengths. The growth of these bands after lengthy irradiation is proportional to the growth of the F band, with a proportionality constant that does not vary greatly with impurity concentration or type. In doped material, however, there is an initial period in which the F band grows without corresponding growth of these ultraviolet bands.

(d) The stability of defects produced by irradiation at 80°K is greater in pure than in doped material. This can be observed by measuring the fraction of F centers that anneals upon warming to room temperature, or by the rate at which the remaining F centers can be bleached at room temperature.

V. POSSIBLE MECHANISMS

In order for impurities to cause a significant enhancement of the measured defect production rates, they must either be able to speed up the primary production mechanism or they must impede recombination processes that go on simultaneously with defect production or during the interval between termination of an irradiation and measurement. Pooley[18] has suggested that the impurity suppression of radiation defect production in the late stage that has been observed at room temperature occurs because impurities supply recombination states for electrons and holes and thus "short-circuit" the primary production mechanism. Unfortunately, such an approach is useless here since we observe an *increase* in production rates. Moreover, at 80°K, holes (V_k centers) are immobile and cannot travel to impurity sites to combine with electrons trapped there. The observations reported here—that the ultraviolet bands and the defect stability depend upon the impurity content—suggest most strongly that the effect of impurities is not simply one of changing the *rate* of the primary production mechanism. If there were only an enhanced primary production rate, the damage product would be the same in all samples and we would not observe shifts in the intrinisic ultraviolet absorption band, or of a lowered defect stability in doped material. Thus, as previously mentioned,[1] we need to consider secondary processes, i.e., what happens after an ion (or atom) has been ejected from a normal lattice site. These processes can be divided into two extreme classes, depending upon whether or not the ejected ion (atom) remains correlated with its vacancy of origin. If it does, then the probability of producing a stable defect P is simply the product of the probability P_e of ejecting an ion times the probability P_s that these defects remain apart. P_s in this case would not depend upon the number of F centers already produced, but could be modified by doping, perhaps by way of impurity-produced lattice strains. If, on the other hand, a significant fraction of the ejected ions (atoms) interacted with defects other than their vacancies of origin, P_s would become a complicated function of the impurity and vacancy concentrations.

The measurements of thermal annihilation of α centers by interstitial ions[19] show that the great majority of the charged Frenkel defects produced at liquid-helium temperature in KBr recombine directly, but that a few percent separate far enough to lose correlation, so that they recombine by a second-order reaction. It is difficult to extrapolate such results to KCl irradiated at 80°K, but one expects most of the F-center–H-center pairs to be uncorrelated, since their average distance of separation should be greater than that for α-center–interstitial-ion pairs created at 5°K.[20]

In a previous publication[1] it was assumed implicitly that the Frenkel pairs were uncorrelated. However, there was no attempt at quantitative fitting. Recently Farge *et al.*[21] have calculated the shape of the defect production curve for LiF at room temperature by assuming uncorrelated Frenkel defects and mobile interstitials which can recombine with vacancies or can be trapped at sinks. They found an approximate solution to the system of rate equations:

$$\begin{aligned} di/dt &= A - Biv - CNi, \\ dv/dt &= A - Biv, \end{aligned} \tag{1}$$

where i and v are the interstitial and vacancy concentrations during irradiation, and A, B, C, and N are constants. A depends upon the dose rate and defect

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[17] E. Sonder, W. A. Sibley, J. E. Rowe, and C. M. Nelson, Phys. Rev. **153**, 1000 (1967).

[18] D. Pooley, J. Phys. **C1**, 323 (1968).

[19] N. Itoh, B. S. H. Royce, and R. Smoluchowski, Phys. Rev. **137**, A1010 (1965); H. Rüchardt, *ibid.* **103**, 873 (1956).

[20] F. Lüty [Z. Physik **153**, 247 (1958)] has suggested that α-center–interstitial-ion pairs result precisely because the members of the pair are relatively close and the electrostatic field of the interstitial ion prevents the capture of an electron by the vacancy.

[21] Y. Farge, P. Durand, and M. Lambert, J. Phys. Chem. Solids (to be published).

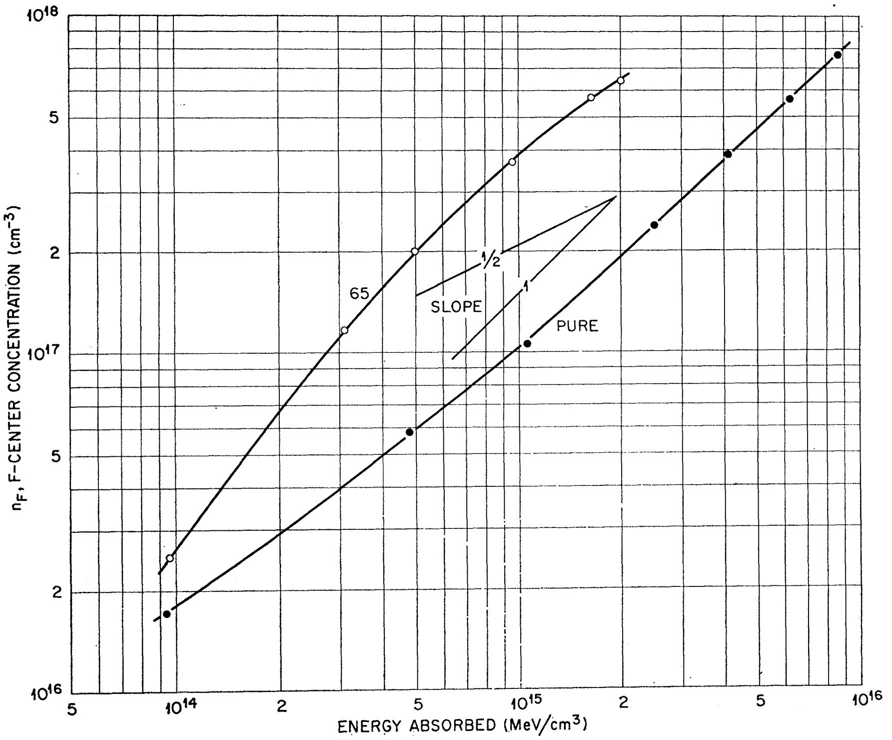

FIG. 11. F-center production versus time, plotted on log-log paper. Experimental curves shown are for pure KCl and heavily (65-ppm) silver-doped material; for comparison, lines with slope $\frac{1}{2}$ and 1 are also shown.

production efficiency; B and C depend upon the interstitial mobility and, respectively, the recombination and trapping cross sections; and N is the sink concentration. For a trapping rate CNi much smaller than the recombination rate Biv, and for times considerably longer than the initial buildup on a steady-state interstitial concentration, the solution yielded a vacancy growth rate inversely proportional to the vacancy (assumed equal to F center) concentration. This would give a growth curve that has a square-root dependence on time, in agreement with the LiF data. Identical assumptions should be valid for our KCl results if the interstitials are not correlated with their vacancies of origin. However, Fig. 11, which is a log plot of the coloring curves for a pure and a heavily silver-doped sample, shows that there is no square-root dependence. In particular, for the pure sample, for which the needed condition $CNi \ll Biv$ is even more reasonable than in doped samples where the trap concentration N is larger, the time dependence is much closer to linear. We have only reproduced one curve for a doped sample in Fig. 11. The other samples behaved similarly; there was no square-root fit.

In addition, an approximately linear growth curve has recently been observed for NaCl irradiated at 80°K.[22] Also for LiF, the square-root dependence on time disappears when the material is irradiated at liquid-nitrogen temperature.[23]

This absence of a square-root time dependence suggests one of two possibilities. Either the parameter CN in Eq. (1) increases with irradiation time, thus compensating for the decrease in interstitial concentration as irradiation progresses, and removing a part of the negative curvature of the coloring curves, or the model, based upon competition of interstitial-vacancy recombination and interstitial trapping, is an oversimplification. A fuller analysis of Eq. (1) and some preliminary measurements of the dose *rate* dependence of defect production[24] tends to support the latter possibility. That is, the model that seems so attractive for explaining the impurity enhancement of color center production may have to be modified.

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[23] Y. Farge (private communication).

[24] E. Sonder (to be published).